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Department of Sciences, Manipal University

III SEMESTER M.Sc. END SEMESTEREXAMINATIONS, NOV/DEC 2015

SUBJECT: Advanced Organic Chemistry [CHM 703]

REVISED CREDIT SYSTEM

Time: 3 Hours MAX.MARKS: 50

Instructions to Candidates:

- ❖ Answer ANY 5 Full questions.
- ❖ Write chemical equations wherever necessary
- **1A.** Justify the following statements;
 - i. Furan is the least aromatic five membered heterocycle when compared to thiophene and pyrrole.
 - ii. Juvenile hormone, Methoprene is considered as a biological pesticide.
 - iii. 1*H*-Azepine is non-aromatic in nature.
- **1B.** Explain the functions of following phytohormones with one example each;
 - i) Auxins
- ii) Cytokinins
- iii) Gibberellins
- **1C.** Discuss the following reactions:
 - i) Reduction of 2-ethenylfuran with raney nickel at 125 °C
 - ii) Halogenation of pyrrole
 - iii) Oxidation of thiirane with sodium metaperiodate
 - iv) Nucleophilic aromatic substitution in trichloro-1,3,5-triazine

3+3+4

- **2A.** Explain the following reactions;
 - i) Thermal cyclization of unsaturated diazo compounds
 - ii) Desulfurization of thietane
 - iii) Nucleophilic aromatic substitution in 1,3,5-triazines
- **2B.** Discuss the following;
 - i. Friedel-Crafts reaction of aziridines
 - ii. Ring opening reaction of oxirane
 - iii. Diels-Alder reaction of 2,3,5,6-tetrazine
- **2C.** What are organophosphorous pesticides? Discuss the synthesis and uses of malathion, mevinphos and phorate.

3+3+4

- **3A.** Justify the following statements;
 - i) 5H-1,2-diazepines show a strong preference to exist as bicyclic tautomers
 - ii) Carbamate pesticides are superior to organochlorine pesticides.
 - iii) Indole is a very weak base.
- **3B.** What are the different types of insect repellants? Explain the synthesis and use of DEET. Why is Icardin preferred over DEET as an insect repellant?

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- **3C.** Explain the synthesis of the following molecules:
 - i) Benzofuran from coumarin
- ii) Paal-Knorr synthesis of thiophene

3+3+4

- Discuss the reaction conditions for the reduction of the following compounds by 4A. catalytic hydrogenation method. (a) butene (b) benzene and (c) cyclohexene
- 4B. An organic compound (C₅H₇OCl) gives compound "B" (C₅H₉OCl) when treated with reagent "A": compound "D" (C₅H₉OCl) when treated with reagent "C" and compound "F" (C₅H₁₁OCl) when treated with reagent "E". Identify "A" to "F".
- Why is it undesirable to use K₂Cr₂O₇ / H₂SO₄ for the oxidation of unsaturated 4C. alcohols and Jones reagent for amino alcohols. Propose the suitable alternative agent for the oxidation of the same.

3+3+4

- Explain the reactivity of lithium aluminium hydride and sodium borohydride. How 5A. do you increase the specificity of a reagent?
- 5B. Write the chemical reaction to explain the concept of temperature effect on the following reactions.
 - (i) Cyclohexanol with K₂Cr₂O₇
 - (ii) Unsaturated alcohol with Jones reagent
 - (iii) Primary alcohol with pyridinium dichromate
- 5C. Explain the four reactions of the free radicals

3+3+4

An aromatic molecule "A" when treated with "P" gives the product "B". Under the 6A. same conditions, same product is also obtained when the starting material is changed to "C". The reagent "P" can also react with "D" to give "E". Identify "A" to "E" and "P"

Reagent	A	В	С	D	Е
NaOH	No	Yes	No	No	No
Bromine water	No	No	No	Yes	No
Lucas reagent	No	No	No	No	Yes
2,4 DNP	No	No	No	No	No

6B. Identify the proper substrate or product

6C. Starting from propene, how do you prepare (a) 1-chloropropane (b) 2-chloropropane (c) 1,2-dichloropropane (d) 1,2-dihydroxypropane (e) CH2=CH-CH2OH and (f) propane

3+3+4

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